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(54) OUTDOOR SPREADING FILM

## (57)Abstract:

PROBLEM TO BE SOLVED: To remarkably improve heat shielding effect in summer by providing a layer containing inorganic oxide fine particles having specific heat ray shielding ability on one surface of a thermoplastic resin film, and providing a layer containing hydrophilic inorganic colloidal particles on the layer and/or an opposite surface of the film.

SOLUTION: When a layer A is formed only one surface of a thermoplastic resin film, a layer B is formed on the layer A surface or a film surface not formed with the layer A or both the surfaces. When the layer A is formed on both the surfaces, a layer B is formed on at least one surface. To form the layer A, inorganic oxide fine particles doped with at least one type 3A, 4A or 5A group metal and heat ray shielding ability are dispersed in liquid-like dispersing medium together with binder, coated and dried to volatilize liquid-like dispersing medium. And, to form the layer B, a composition containing hydrophilic inorganic colloid and binder is coated by using the dispersing medium, dried, and the dispersing medium is volatilized.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The film for outdoor spreading which prepares the layer (A) containing the inorganic oxide particle which has the heat ray electric shielding ability by which at least one sort of a thermoplastics film which belongs to 3A, 4A, and 5A group on one side at least of metals were doped, and comes further to prepare the layer (B) which contains a hydrophilic minerals colloidal particle on the layer and/or the opposite side of a film.

[Claim 2] The film for outdoor spreading according to claim 1 with which a layer (A) uses a constituent with thermoplastics as the binder with a 5-2000nm inorganic oxide particle as mean particle diameter.

[Claim 3] The film for outdoor spreading according to claim 1 or 2 whose rectilinear-propagation light transmission in 555nm is 80% or more.

[Claim 4] The film for outdoor spreading given in the term of either [ whose inorganic oxide particle of a layer (A) is an indium oxide particle by which the tin-oxide particle or tin with which antimony was doped was doped ] claim 1 thru/or the either of 3.

[Claim 5] The film for outdoor spreading given in the term of either [ whose hydrophilic minerals colloidal particles of a layer (B) are a silica and/or an alumina ] claim 1 thru/or the either of 4.

[Claim 6] The film for outdoor spreading given in the term of either [ using a constituent with the hydrophobic acrylic resin with which a layer (B) has glass transition temperature in the range in which it is 35-80 degrees C as a hydrophilic minerals colloidal particle and its binder ] claim 1 thru/or the either of 5.

[Claim 7] The film for outdoor spreading according to claim 6 whose loadings of the hydrophilic minerals colloidal particle in a constituent are four or less [ 0.5 or more ] in a weight ratio to hydrophobic acrylic resin.

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**DETAILED DESCRIPTION****[Detailed Description of the Invention]**

**[0001]**

**[Field of the Invention]** This invention relates to the film for outdoor spreading used for covering of protected horticulture etc. Furthermore, it is related with the film for outdoor spreading which has transparency and has the outstanding thermal insulation nature in detail.

**[0002]**

**[Description of the Prior Art]** In the protected horticulture from the former, the house covering material generally used makes a visible ray penetrate as much as possible for the purpose of securing intensity of radiation required for the improvement in heat retaining property and photosynthesis of a winter season, for example, lucite films, such as a polyvinyl chloride, polyolefine, and polyethylene terephthalate, are used. The inside of a house serves as an elevated temperature from early summer between early autumn through midsummer for the purpose of the cultivation disposition top of a winter season, and, as for the synthetic-resin film of these former, protected horticulture is difficult. Therefore, by using the protection-from-light network and cheesecloth as a curtain of lining or an outside flare, and interrupting solar radiation (visible-ray \*\*\*\*) about 30 to 80%, the case of the flowering plants of perennation with the need of passing summer reduces the solar radiation energy penetrated in a house, and is suppressing the rise of the temperature in a house. The case of flowering plants has a problem of the spindly growth of the vegetation by protection from light, although the required quantity of light can grow at least.

**[0003]** Moreover, although air conditioning in a house is also performed as a countermeasure to heat of summer, like [ of Japan ], under a heat-and-high-humidity environment, the air conditioning by Myst has aggravation of the work environment which originates in vegetation getting wet, and disease tends to generate, and is depended humidly, and the trouble that the effectiveness is also insufficient, and has not spread further. On the other hand, in the house which solar radiation pours, since air conditioning effectiveness is very low, air conditioning by the refrigerator is also seldom performed. On the other hand, about cultivation of the fruit vegetables of summer, on crop physiology and quality, since protection from light is impossible, in a southwest warm district, cultivation of the fruit vegetables of summer by protected horticulture is hardly performed, but also in a northeast or the cool ground in Hokkaido, the inside of a house serves as an elevated temperature, and quality and work environment pose a problem under covering of a bright film summer. Then, a visible ray is made to penetrate as much as possible, and the covering material of the type which cuts a heat ray (namely, near infrared ray) as much as possible is called for.

**[0004]** The charge of an infrared reflector which vapor-deposited the very thin metal layer on the front face of a synthetic-resin film (JP,59-13325,B), Although the amount of solar-radiation energy which will be penetrated if the light is intercepted since the solar radiation energy from the sun has a near infrared ray field in a light field and has about 50% of the amount of energy in an infrared field about 50% although the film for agriculture (JP,7-274738,A) which used the hologram which reflects a near infrared ray and infrared radiation combining the synthetic-resin film is proposed can be reduced easily, there is a problem that where of the amounts of lights run short. Therefore, it is desirable to absorb or reflect the light of a near infrared ray field positively in solar radiation energy (electric shielding), and scouring a heat ray absorbent or a heat ray reflective agent to a synthetic-resin film or applying are performed.

**[0005]**

**[Problem(s) to be Solved by the Invention]** As an approach which scoured the particle which has heat ray electric shielding ability, for example, tungsten hexachloride, Blending a heat ray reflective agent or heat ray absorbents, such as the second copper of sulfuration, near infrared ray absorption coloring matter of an aminium system, and a metal complex compound JP,4-45546,B, JP,58-56533,B, JP,62-54143,B, JP,50-51549,A, JP,54-25060,B, JP,1-114801,B, It is proposed by JP,2-17306,A, JP,3-215561,A, JP,3-161644,A, JP,6-73197,A, JP,8-81567,A, etc. Moreover, a binder

solution is made to distribute a tin-oxide particle as an approach which applied the heat ray reflective agent or the heat ray absorbent. The heat ray screen which whose visible-ray permeability which comes to produce a film on a transperence base material is high, and is moreover excellent in heat ray electric shielding nature (JP,6-262717,A), The near infrared ray absorptivity film (JP,7-100996,A) which carried out the laminating of the inorganic substance near infrared ray absorption layer which consists of the solid solution of the organic substance near infrared ray absorption layer and tin oxide which become a polyethylene terephthalate film from the amino compound, and antimony oxide is proposed.

[0006] However, by the type (type which blended or applied the heat ray absorbent) which absorbs a heat ray, the base material film absorbed the heat ray, the temperature of a base material film rose, reradiation of the heat from a base material film arose, the temperature in a house was raised, and there was a problem of becoming an opposite effect rather. Moreover, in order to have made the visible ray penetrate as much as possible and to have controlled the temperature rise of the summer in the house for agriculture also by the type which reflects a heat ray, heat ray electric shielding ability was not yet enough.

[0007]

[Means for Solving the Problem] this invention persons examined wholeheartedly the film which is under this background, and penetrates a visible ray as a film for outdoor spreading, and covers a heat ray that the film for outdoor spreading which raised the electric shielding engine performance further should be offered. Consequently, this invention persons checked heightening the thermal insulation effectiveness of a heat ray absorbent further by the latent heat of vaporization of this moisture paying attention to the layer containing a minerals colloid sol incorporating the moisture in air positively. That is, when the humidity in a house is low, the amount of [ which was incorporated on the base material front face ] air Nakamizu evaporates promptly, it takes the latent heat of vaporization, prevents overheating of a base material film, and reduces reradiation of the heat ray from a base material film. When the inside of a house is humid, the water screen arises on a film front face and the water screen always flows down a base material side, the heat of a base material film is taken, further, the specific heat of the water screen can be high, the rise of base material temperature can be prevented, and reradiation from a base material film can be reduced.

[0008] The place which carries out a deer and which is made into the summary of this invention prepares the layer (A) containing the inorganic oxide particle which has the heat ray electric-shielding ability by which at least one sort of a thermoplastics film which belongs to 3A, 4A, and 5A group on one side at least of metals were doped, and consists in the film for outdoor spreading which comes to prepare the layer (B) which contains a hydrophilic minerals colloidal particle on the layer and/or the opposite side of a film further.

[0009]

[Embodiment of the Invention] In this invention, a heat ray means the near infrared ray of the range of 200-2600nm wavelength, and electric shielding means reflection or absorption. Hereafter, this invention is explained to a detail. Any are sufficient as long as it is resin generally used for film shaping as thermoplastics which constitutes the film for outdoor spreading of this invention. Specifically, the blend object of these polymers, such as a polymer independent [ monomers, such as a vinyl chloride, ethylene, a propylene, acrylic ester, methacrylic ester, and fluoride ethylene, ] or mutual [ these ] or a copolymer of at least one sort of these monomers and the monomers (for example, vinyl acetate, a vinylidene chloride, etc.) in which other copolymerization is possible, fluorine-containing resin, polyester, and a polyamide, is raised. In these, from viewpoints, such as weatherability, light transmission nature, economical efficiency, and reinforcement, vinyl chloride system resin (namely, the copolymer which contains a polyvinyl chloride and a vinyl chloride 50% of the weight or more), and ethylene system resin (namely, the copolymer which contains polyethylene and ethylene 50% of the weight or more) are suitable, and are polyethylene terephthalate and a fluororesin most advantageously.

[0010] When using polyethylene terephthalate, although the non-extended thing was also extended by two shafts, if a film is said from the point of the reinforcement of a film, what was extended by two shafts is desirable. When extending on two shafts, length, width, and the thing extended 2.0 to 5.0 times are desirable. Since the reinforcement of a product does not become that draw magnification is less than 2.0 times with sufficient thing, by the thing exceeding 5.0 times, the reinforcement of a product becomes sufficient thing preferably, but since fabrication operation becomes difficult, it is not desirable. The 2.5 to 4.0 times as many range of especially draw magnification as this is [ 2 shaft orientations ] desirable respectively. Especially the method of manufacturing a biaxially oriented film may depend on what kind of approach [ it not being limited, and being alike serially, for example, extending on every direction 2 shaft at coincidence etc. ] learned conventionally.

[0011] The thermoplastics film concerning the film for outdoor spreading of this invention has that desirable whose thickness is 0.01-0.3mm. Since a film will become hard and it will be hard coming to deal with it if the reinforcement of

a product does not become that thickness is less than 0.01mm with sufficient thing and 0.3mm is exceeded, it is not desirable. Amount combination of the addition assistants, such as the plasticizer of the common knowledge added by usual thermoplastics, lubricant, a thermostabilizer, an organic phosphorus acid metal salt, an antifogger, anti-fog agent, an ultraviolet ray absorbent, light stabilizer, a coloring agent, a stabilizer, and an antioxidant, can usually be carried out at these thermoplastics if needed.

[0012] As lubricant thru/or a thermostabilizer, KIRETA like the fatty-acid system lubricant generally used for the film for outdoor spreading, fatty-acid amide system lubricant, ester system lubricant, polyethylene wax, a liquid paraffin, and an organic phosphite compound, phenols, beta-diketone compound, etc. are raised. Specifically, there is [ \*\*\*\* / 7th / of - of one line 12th line / of JP,62-53543,B ] a compound of a publication etc.

[0013] The following is raised as an ultraviolet ray absorbent. 2-ethylhexyl-2-cyano which is a cyanoacrylate system ultraviolet ray absorbent - 3, 3'-diphenyl acrylate, ethyl-2-cyano - 3, 3'-diphenyl acrylate, etc. The 2-hydroxy-4-methoxybenzophenone which is a benzophenone system ultraviolet ray absorbent, 2, 4-dihydroxy benzophenone, 2-hydroxy-4-n-octoxybenzophenone, A 2-hydroxy-4-methoxy-2'-carboxy benzophenone, 2, 2'-dihydroxy -4, a 4'-dimethoxy benzophenone, a 2-hydroxy-4-benzoyloxy benzophenone, 2 and 2'-dihydroxy-4-methoxybenzophenone, a 2-hydroxy-4-methoxy-5-sulfone benzophenone, 2, 2', and 4 and 4 -- a - tetra-hydroxy benzophenone, and '2, 2' - dihydroxy -4 and 4' - dimethoxy benzophenone, a 2-hydroxy-5-KURORU benzophenone, screw-(2-methoxy-4-hydroxy-5-benzoyl phenyl) methane, etc.

[0014] 2-(2'-hydroxyphenyl) benzotriazol which is a benzotriazol system ultraviolet ray absorbent, 2-(2'-hydroxy-5'-methylphenyl) benzotriazol, 2-(2'-hydroxy-5-methylphenyl)-5-carboxylic-acid butyl ester benzotriazol, 2-(2'-hydroxy-5'-methylphenyl)-5, 6-dichloro benzotriazol, 2-(2'-hydroxy-5'-methylphenyl)-5-ethyl sulfone benzotriazol, 2-(2'-hydroxy-5'-t-buthylphenyl)-5-chlorobenzo triazole, 2-(2'-hydroxy-5'-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-5'-aminophenyl) benzotriazol, 2-(2'-hydroxy-3', 5'-dimethylphenyl) benzotriazol, 2-(2'-hydroxy-3', 5'-dimethylphenyl)-5-methoxybenzo triazole, 2-(2'-methyl -4'-hydroxyphenyl) benzotriazol, 2-(2'-stearyl oxy--3', 5'-dimethylphenyl)-5-methyl benzotriazol, 2-(2'-hydroxy-5-carboxylic-acid phenyl) benzotriazol ethyl ester, 2-(2'-hydroxy-3'-methyl -5'-t-buthylphenyl) benzotriazol, 2-(2'-hydroxy-3', 5'-G t-buthylphenyl)-5-chlorobenzo triazole, 2-(2'-hydroxy-3'-t-butyl -5'-methylphenyl)-5-chlorobenzo triazole, 2-(2'-hydroxy-5'-methoxyphenyl) benzotriazol, 2-(2'-hydroxy-3', 5'-G t-buthylphenyl)-5-chlorobenzo triazole, 2-(2'-hydroxy-5'-cyclohexyl phenyl) benzotriazol, 2-(2'-hydroxy-4', 5'-dimethylphenyl)-5-carboxylic-acid benzotriazol butyl ester, 2-(2'-hydroxy-3', 5'-dichloro phenyl) benzotriazol, 2-(2'-hydroxy-4', 5'-dichloro phenyl) benzotriazol, 2-(2'-hydroxy-3', 5'-dimethylphenyl)-5-ethyl sulfone benzotriazol, 2-(2'-hydroxy-4'-octoxy phenyl) benzotriazol, 2-(2'-hydroxy-5'-methoxyphenyl)-5-methyl benzotriazol, 2-(2'-hydroxy-5'-methylphenyl)-5-carboxylate benzotriazol, 2-(2'-acetoxyl -5'-methylphenyl) benzotriazol, etc.

[0015] Furthermore, these cyanoacrylate system, a benzophenone system, the quantity object of a benzotriazol system ultraviolet ray absorbent, and a polymer are raised. It is desirable to use a benzophenone system ultraviolet ray absorbent or a benzotriazol system ultraviolet ray absorbent especially. these ultraviolet ray absorbents -- one sort or two sorts or more -- you may use together -- the amount used -- per [ 0.01 ] thermoplastics 100 weight section - 5 weight sections -- it is 0.05 - 2 weight section preferably.

[0016] With the inorganic oxide particle which has the heat ray electric shielding ability by which at least one sort of metals which belong to 3A, 4A, and 5A group who constitute a layer (A) in this invention were doped To for example, metallic oxides, such as indium oxide, tin oxide, a germanium dioxide, and a zinc oxide The metal belonging to 3A, 4A, and 5A group is made to dope, conductivity is given, the indium oxide (ITO) by which tin was doped, the tin oxide (ATO) by which antimony was doped, the germanium dioxide with which the gallium was doped specifically raise, and it is \*\*\*\*. Moreover, two or more sorts of metals belonging to 3A, 4A, and 5A group may be made to dope.

[0017] Since surface scattered reflection also becomes remarkable and visible-ray permeability falls, it is not desirable, except that surface roughness will fall, and the particle size of the primary particle of these inorganic oxide particle can perform a crater-like crater and a projection and will become a poor appearance, if mean particle diameter becomes a coarse-grain object exceeding 2000nm. Therefore, a thing 2000nm or less has the desirable mean particle diameter of an inorganic oxide particle. Moreover, in the film after a layer (A) and (Layer B) shaping, when the object crop range is taken into consideration, as for the addition of an inorganic oxide particle, it is more desirable [ it should be adjusted so that the permeability of a light field (representing permeability in 555nm) may become 60% or more, but ] to adjust to loadings which become 80% or more with a visible-ray permeability value. These inorganic oxide particle may use one sort or several sorts for coincidence. Moreover, even if it uses together metal complexes, such as organic compounds, such as an anthraquinone derivative, and a phthalocyanine compound, a naphthalocyanine compound, a squarylium compound, a thiourea compound, a potato NIUMU system compound, an acetylene series compound, or chromium, cobalt, and copper, it does not interfere.

[0018] the forced drying in order to form this layer (A), after applying what distributed the inorganic oxide particle in the liquefied dispersion medium with the binder on the front face of a thermoplastics film -- or what is necessary is to season naturally and just to vaporize a liquefied dispersion medium What is necessary is just to use thermoplastics as a binder. Although acrylic resin, vinyl chloride vinyl acetate system resin, polyethylene system resin, vinyl chloride system resin, vinylidene-chloride system resin, polyurethane system resin, polycarbonate system resin, styrol system resin, vinyl acetate system resin, unsaturated polyester system resin, etc. are raised, specifically, especially acrylic resin is suitable.

[0019] As an approach of carrying out a forced drying, a hot-air-drying method, the infrared radiating method, etc. are employable. Moreover, as an approach of applying, it is good in itself by any well-known approaches, such as the roll coat method, a dip coating method, the brush applying method, a spray coating method, the bar coat method, and the knife coat method.

[0020] When a film front face and an adhesive property with a layer (A) are not enough, before applying a layer (A), plasma treatment may be performed to a film front face, corona discharge treatment may be performed, or a film front face may be reformed by approaches, such as spreading of a suitable anchoring agent. The film for outdoor spreading of this invention forms a layer (B) on the opposite side of the film in which the field [ in which the layer (A) was formed ] top, or the layer (A) was formed. That is, a layer (B) may be formed in the film front-face top which does not form (Layer A) side top or the layer (A), or both sides when a layer (A) is formed only in film one side. What is necessary is just to form a layer (B) in the whole surface at least, when a layer (A) is formed in film both sides.

[0021] As a hydrophilic minerals colloidal particle which constitutes a layer (B) in this invention, a silica, an alumina, water-insoluble nature lithium silicate, an iron hydroxide, tin hydroxide, titanium oxide, a barium sulfate, etc. are raised, for example, and these are various approaches and are used in the form of the hydrosol distributed in water or a hydrophilic medium. A silica sol and alumina sol are desirable especially. These may be used independently or may be used together. As a minerals colloid sol to be used, the thing of the range the solid-state mean particle diameter of whose is 5-100mmicro is desirable. As long as it is within the limits of this, you may use combining two or more sorts of colloid sols from which mean particle diameter differs. If mean particle diameter exceeds 100mmicro, since the inclination which a paint film devitrifies white not only comes out, but the thermal insulation effectiveness falls, it is not desirable. Moreover, when not fulfilling 5mmicro, there is a possibility that the stability of a minerals colloid sol may be missing.

[0022] As for a layer (B), it is desirable that it is the constituent which uses the hydrophobic acrylic resin in the range of 35-80-degree C glass transition temperature as a binder. As for a hydrophilic minerals colloidal particle, it is desirable to make the loadings or less [ 0.5 or more ] into four by the weight ratio to this acrylic resin. That is, when not fulfilling 0.5, sufficient thermal insulation effectiveness cannot be demonstrated. Moreover, when exceeding 4, since the paint film the thermal insulation effectiveness not only does not improve in proportion to loadings, but formed when mold goods are transparent nebula-izes, light transmission is reduced, and a paint film is coarse and becomes easy to become brittle, it is not desirable.

[0023] The homopolymer or copolymer with which glass transition temperature carried out the polymerization of alpha which copolymerizes [ at least 60 % of the weight and these, and ] the mixture of acrylic-acid (meta) alkyl ester or (meta) acrylic-acid alkyl ester, and alkenylbenzenes, and the 0 - 40 % of the weight of the beta-ethylenic unsaturated monomers as \*\*\*\*\* acrylic resin to the range which is 35-80 degrees C, and was obtained in it is desirable.

[0024] (Meta) With acrylic-acid alkyl ester It is alkyl ester of an acrylic acid or a methacrylic acid. Specifically for example Acrylic-acid methyl ester, ethyl-acrylate ester, acrylic-acid-n-propyl ester, Acrylic-acid isopropyl ester, acrylic-acid-n-butyl ester, Acrylic-acid-2-ethylhexyl ester, acrylic-acid DESHIRU ester, Methacrylic acid methylester, ethyl methacrylate ester, methacrylic-acid-n-propyl ester, Methacrylic-acid isopropyl ester, methacrylic-acid-n-butyl ester, methacrylic-acid-2-ethylhexyl ester, methacrylic-acid DESHIRU ester, etc. are raised. Generally The alkyl methacrylate ester whose carbon number of the acrylic-acid alkyl ester whose carbon number of an alkyl group is 1-20 pieces, and/or an alkyl group is 1-20 pieces is used.

[0025] As alkenylbenzenes, styrene, alpha methyl styrene, vinyltoluene, etc. are raised, for example. Although it changes also with amount of alpha and beta-ethylenic unsaturated monomer used in using the mixture of alkenylbenzenes and acrylic-acid (meta) alkyl ester, it is good to usually (meta) make the operating rate of acrylic-acid alkyl ester into 10 % of the weight or more, and what contains the alkenylbenzenes occupied in hydrophobic acrylic resin in 70 or less % of the weight of the range is good.

[0026] As alpha in which the mixture of the aforementioned (meta) acrylic-acid alkyl ester, or a this and alkenylbenzenes and copolymerization are possible, and a beta-ethylenic unsaturated monomer For example, an acrylic acid, a methacrylic acid, a maleic acid, a maleic anhydride, a fumaric acid, A crotonic acid, alpha, such as an itaconic

acid, alpha like a beta-ethylene nature unsaturated-carboxylic-acid:ethylene sulfonic acid, beta-ethylene nature partial saturation sulfonic-acids:2-acrylamide-isobutane acid;alpha, and beta-ethylene nature partial saturation phosphonic acid : An acrylic acid or hydroxyl-group content vinyl monomers [, such as hydroxyethyl of a methacrylic acid, ]: -- acrylonitrile: -- acrylamide; -- there is glycidyl ester of an acrylic acid or a methacrylic acid. These monomers may be used independently, or two or more sorts of concomitant use is sufficient as them, and they can be used in 0 - 40% of the weight of the range.

[0027] The hydrophobic acrylic resin in this invention has a desirable thing within the limits the glass transition temperature (Tg) of whose is 35-80 degrees C. Such a thing of Tg is obtained by the class of monomer to be used, and selection of the amount used (loadings). If Tg of the acrylic resin used carrying out a deer exceeds 80 degrees C, when a transparent uniform paint film will be hard to be obtained and Tg will not fulfill 35 degrees C, a minerals colloidal particle condenses several order and it is easy taking an uneven distributed condition, and since a minerals colloidal particle is dropped out and spilt out from a base material front face with the passage of time since fixing over the spreading base material of a minerals colloidal particle is not enough, and the improvement effectiveness in the thermal-insulation engine performance is spoiled, it is not desirable.

[0028] Although hydrophobic acrylic resin is usually used as a drainage system emulsion, even if it uses the drainage system emulsion obtained by the polymerization in the inside of a drainage system medium in each monomer in that case as it is, what added and diluted the liquefied dispersion medium to this thing further may be used, and what carried out judgment extraction of the polymer produced by the above polymerizations, and the liquefied dispersion medium was made to re-distribute this, and was made into the drainage system emulsion may be used.

[0029] In order to raise the water wettability of a layer (B), the electrolyte of monovalence may be added to the constituent of a layer (B). Specifically, weak electrolytes, such as strong electrolytes, such as a hydroxide of a nitric acid, alkali metal, or alkaline earth metal and mineral salt, an organic acid, and an organic base, can be raised. As a strong electrolyte, mineral, such as inorganic hydroxides, such as inorganic acids, such as a nitric acid and a hydrogen bromide, a potassium hydroxide, a lithium hydroxide, and a sodium hydroxide, a sodium bromide, a sodium iodide, a potassium bromide, a potassium nitrate, a rubidium bromide, an iodation rubidium, a cesium bromide, a cesium iodide, a silver nitrate, an ammonium bromide, ammonium iodide, a hydrogen chloride, an ammonium chloride, a sodium chloride, and potassium chloride, is raised. As a weak electrolyte, an acetic acid, ammonium acetate, potassium acetate, sodium acetate, etc. are raised.

[0030] these electrolytes -- one sort -- or two or more sorts may be used together. The addition of the electrolyte of such monovalence is 0.01 - 30 weight section to the hydrophilic minerals colloidal particle 100 weight section, and its 0.01 - 10 weight section is especially desirable also in 0.01 - 20 weight section. When an electrolyte is a liquid, the weight of an active principle is said 100%. Furthermore, in a layer (B), additives of common use, such as a defoaming agent, a plasticizer, a film formation assistant, a thickener, a pigment, a pigment agent, light stabilizer, and an ultraviolet ray absorbent, are mixable if needed.

[0031] the constituent which contains a hydrophilic minerals colloidal particle and a binder in order to form a layer (B) - - as a liquefied dispersion medium -- mixture with water or water, a hydrophilic property, or a water miscibility solvent -- using -- dispersion liquid -- carrying out -- this -- the front face of a thermoplastics film, or the front face of a layer (A) -- applying -- a forced drying -- or what is necessary is to season naturally and just to vaporize a liquefied dispersion medium As a solvent of a hydrophilic property thru/or water miscibility, ring type alcohols:cellosolve acetate:ketones [, such as polyhydric-alcohol:benzyl alcohol, ], such as monohydric-alcohol:ethylene glycol, such as methyl alcohol, ethyl alcohol, and isopropyl alcohol, a diethylene glycol, and a glycerol, are raised. These may be used independently or may be used together.

[0032] Moreover, it is desirable to blend a cross linking agent with dispersion liquid. By the cross linking agent, acrylic resin can construct a bridge and a water resisting property can be raised. As a cross linking agent, although phenol resin, amino resin, amine compounds, aziridine compounds, azo compounds, isocyanate compounds, epoxy compounds, and silane compounds are raised, amine compounds, aziridine compounds, and epoxy compounds are especially suitable. As an approach of carrying out a forced drying, a hot-air-drying method, the infrared radiating method, etc. are employable. Although the heating temperature when carrying out a forced drying is determined by the applied constituent, the range of it is 70-200 degrees C preferably 50-250 degrees C.

[0033] As an approach of applying, it is good in itself by any well-known approaches, such as the roll coat method, a dip coating method, the brush applying method, a spray coating method, the bar coat method, and the knife coat method. the coating weight of the solid after applying dispersion liquid on the surface of a film, drying and vaporizing a liquefied dispersion medium -- usually -- 0.01 - 10 g/m2 -- desirable -- 0.1 - 5 g/m2 It is the range.

[0034] When the adhesive property of a film front face and a layer (B) is not enough, before applying a layer (B), a film



front face may be reformed by performing plasma treatment to a film front face, or performing corona discharge treatment etc. Moreover, what is necessary is just to give an anchor coat etc. on a layer (A), before applying dispersion liquid when the adhesive property of a layer (A) and a layer (B) is not enough. In case spreading use of the film for outdoor spreading of this invention is carried out, it spreads so that a layer (B) may become inside a house or a tunnel about the field in which the layer (B) was formed in the case of the film with which only one side was formed. It does not interfere, even if it prepares the enveloping layer which consists of other resin, for example, acrylic resin, fluorine system resin, or polyolefine system resin on the field in which the layer (B) of this film is not formed in order to improve the protection-against-dust nature, the fog resistance, weatherability, and blocking resistance of the film for outdoor spreading concerning this invention and which is not.

[0035]

[Effect of the Invention] Since the film for outdoor spreading concerning this invention is excellent in transparency and its thermal insulation effectiveness in the house for agriculture of summer improves by leaps and bounds according to the synergistic effect of a layer (A) and a layer (B), the utility value as a film for outdoor spreading is very large.

[Example] Hereafter, although this invention is explained to a detail based on an example, this invention is not limited to the following examples, unless the summary is exceeded.

Examples 1-8, the examples 1-8 of a comparison [0036] (1) It blended to the (Preparation i) polyethylene terephthalate film polyethylene terephthalate (limiting viscosity measured at 25 degrees C is thing of 0.65, using o-chlorophenol as solvent) 100 weight section of a base film by the blending ratio of coal which showed the ultraviolet ray absorbent shown in Table -1 in this table. After carrying out stirring mixing of each compound for 10 minutes by the super mixer, with the conventional method, the extension temperature of 65 degrees C, and 3.5 times as many draw magnification as this, subsequently to a longitudinal direction, biaxial stretching was serially carried out to melting extrusion and a lengthwise direction by the extension temperature of 65 degrees C, and 3.5 times as many draw magnification as this, and the biaxial oriented film with a thickness of 0.15mm was manufactured to them. The consistencies of this film were 1.37 g/cm<sup>3</sup>.

[0037] (ii) As opposed to the elasticity vinyl chloride system resin film polyvinyl chloride (polymerization degree = 1300) 100 weight section, 50 weight sections and tricresyl phosphate for dioctyl phthalate Five weight sections, Two weight sections and a Ba-Zn system powder stabilizer for 2 weight sections and a Ba-Zn system liquefied stabilizer One weight section, [ an epoxy resin ] Weighing capacity of the 0.1 weight section is carried out for the ultraviolet ray absorbent which showed sorbitan monopalmitate in the 1.5 weight section and Table -1. After carrying out stirring mixing of these for 10 minutes by the super mixer, it kneaded on the roll heated at 165 degrees C, and the transparent elasticity vinyl chloride system resin film with a width of face [ of 100cm ] and a thickness of 0.10mm was manufactured with L type calender equipment.

[0038] (iii) On one side of a fluororesin film ethylene-tetrafluoroethylene copolymerization resin film (the tefzel AS by E. I. du Pont de Nemours & Co., thickness of 64 micrometers), corona treatment was performed by discharge voltage 120V and discharge current 4.7A, line speed 5 - 15 m/min.

[0039] (iv) Using 100mmphi (Product made from Plastic \*\*\*\*) for the three-layer die as three layer inflation-molding equipment of polyolefine system films, the extruder manufactured the laminated film with a thickness of 0.15mm it sets the middle class to 40mmphi (Product made from Plastic \*\*\*\*), setting an ectosarc layer as 30mm phi (Product made from Plastic \*\*\*\*) two sets, and it is thin from the following combination in a part for 5m/in the molding temperature of 160 degrees C the blow ratio 2.0, and taking over rate

[0040]

[Outer layer] Raw material resin (EVA (5% of VA components)) The 100 weight sections Organic phosphorus acid metal salt (phosphoric-acid mono-octadecyl zinc salt) 0.5 \*\* hindered amine (MARK LA-57) 0.5 \*\* ultraviolet ray absorbent 0.5 \*\* sorbitan monostearate 0.5 \*\* [0041]

[Inner layer] Raw material resin (EVA (15% of VA components)) The 100 weight sections Organic phosphorus acid metal salt (phosphoric-acid mono-octadecyl zinc salt) 0.5 \*\* hindered amine (MARK LA-57) 0.5 \*\* ultraviolet ray absorbent 0.5 \*\* sorbitan monostearate 0.5 \*\* hydrotalcites 15 \*\* [0042]

[Table 1]



表-1

フィルムNo	(重量部)	1	2	3	4	5	6	7	8	9	10	11	12
フィルム素材	メチルメタクリレートフィルム	○	○	○	○					○			
	フッ素樹脂フィルム					○	○				○		
	シリル化ビニルフィルム							○				○	
	シリルエーテル系フィルム								○				○
UV剤	2,4-ジ-tert-ブチル-6-メチル-5-ヒドロキシベンゾフェノン		0.5	0.5					0.1				0.1
	2-tert-ブチル-6-メチル-5-ヒドロキシ-4-オクタメチルベンゾフェノン	1.0						0.1		1.0		0.1	
	2(2'-tert-ブチル-6'-メチル-5'-ヒドロキシ-4'-オクタメチルベンゾフェノン)-5				0.5								

## [0043] (2) Layer (A)

(i) The inorganic oxide of the class shown in the preparation table -2 of a layer (A) constituent was blended with the acrylic resin solution (the methyl methacrylate 50 weight section, butyl methacrylate 30 weight section, and 2-hydroxyethyl methacrylate 20 weight section) with the loadings shown in Table -2, and M-P which is a layer (A) constituent was prepared. In addition, ITO is the Sumitomo Osaka Cement make and ultrafine particles ITO and ATO are the Sumitomo Osaka Cement make and an ultrafine particle ATO.

[0044]

[Table 2]

表-2 (層A)

層AのNo	(重量部)	M	N	O	P
アクリル系樹脂		15	15	15	15
ITO (平均粒径 0.5 $\mu$ m)		5.0			
ATO (平均粒径 0.5 $\mu$ m)			5.0		
酸化亜鉛 (平均粒径 2 $\mu$ m)				5.0	
雲母チタン (平均粒径 6 $\mu$ m)					5.0
液状分散媒 (メチルエチルケトン)		80	80	80	80

[0045] (ii) By the bar coat method, applied the class product obtained by (2)-(i) so that the coverage after desiccation might serve as 10 g/m<sup>2</sup> as solid content, and one side (on the field where surface preparation was carried out in the case of the fluorine film) of each film obtained by formation (1) of a layer (A) was made to pile up for 1 minute into 130-degree C hot blast, and the solvent was dispersed on it.

## [0046] (3) Layer (B)

(i) The polyoxyethylene lauryl ether 2 weight section and the water 80 weight section were taught to the preparation 4 Thu opening flask of binder resin (acrylic resin), it heated to 60 degrees C under the nitrogen gas air current, the ammonium persulfate 0.5 weight section was added here, and the mixture 100 weight section of each monomer further shown in Table -1 was dropped over 3 hours. Although the reaction temperature in this case was held in the range of 60-70 degrees C, it cooled, after holding after dropping termination to this temperature requirement for 2 hours, and the acrylic resin emulsion was obtained. The glass transition temperature of each resin is as having been shown in Table -3, and is the value computed by the degree type.

[0047]  $(1/T_g) = (W1 / T_{g1}) + (W2 / T_{g2}) + \dots + (W_n / T_{gn})$  (inside of a formula, Tg: glass transition temperature of hydrophobic acrylic resin (K))

Tg1 and Tg2 .. Tgn : Each components 1 and 2 ... Glass transition temperature of the homopolymer of n (K)

W1 and W2 .. Wn : Each components 1 and 2 .... Weight fraction of n It is shown respectively.

[0048] (ii) -- layer (B) constituent adjustment (3)-- the component of the class shown in Table -3, the minerals colloid sol of an amount, and others was blended with the water dispersion of the acrylic resin manufactured by (i), and various layer (B) constituents were adjusted to it.

(iii) On the field in which the layer (A) of the film obtained by formation (2) of a layer (B) was formed, by the bar coat method, applied the various constituents obtained by (3)-(ii) so that the coverage after desiccation might serve as 0.5 g/m<sup>2</sup> as solid content, and it was made to pile up for 1 minute into 80-degree C hot blast, and the solvent was dispersed.

[0049]

[Table 3]

表-3 (層B)

層BのNo			(重量部)		A	B	C	D	E	F	G	H
アクリル組成	(メタ)アクリル酸 アルキルエステル類 及び アクリルベンゼン類	メタクリル酸メチル	15	60	65	60	15	60	15	60		
		メタクリル酸n-ブチル		40	24	40		40		40		
		アクリル酸エチル	24				24		24			
		スチレン	50		10		50		50			
	$\alpha, \beta$ - エチレン性不飽 和単量体	アクリル酸	1		1		1		1			
		メタクリル酸-2-ヒドロキシエチル	10				10		10			
	アクリル系樹脂のT <sub>g</sub> (℃)			60	65	83	65	60	65	60	65	
層Bの組成	アクリル系樹脂 *1		2.5	2.0	2.0	2.5	2.5	2.0	2.5	2.0		
	コロイダルシリカ (平均粒径45nm)		2.5		3.0	2.5	2.5		2.5			
	アルミナ (平均粒径30nm)			3.0				3.0		3.0		
	架橋剤 *2			0.05	0.05	0.05		0.05		0.05		
	液状分散媒 水/エタノール=3/1		95	95	95	95	95	95	95	95		

## Notes

\*1 In weight number of copies of acrylic resin, weight number of copies of a minerals colloid sol showed minerals particle weight, and weight number of copies of a cross linking agent showed the weight section of solid content for the amount of polymer solids in a drainage system emulsion respectively.

\*2 For B, F, and H, C and D are a large day about the aziridine system compound made from mutual \*\*\*\*. The bisphenol A type epoxy compound made from This Ink Chemistry was used.

[0050] (4) the approach indicated below about evaluation profit \*\*\*\* each film estimated various kinds of properties, and the result was shown in Table -4.

(i) Using the visible-ray permeability recording spectrophotometer (Hitachi 330 mold), 60phi integrating sphere was used and the total light transmission in 555nm was measured.

(ii) Using the rate recording spectrophotometer of heat ray cutoff (Hitachi 330 mold), 60phi integrating sphere was used, and the total light transmission in 200-2600nm was measured, and the wavelength dependency data of the solar radiation energy from the sun were set, and the ratio with the solar radiation energy which there are no solar radiation energy and base material which are intercepted by the base material, and is received directly showed.

[0051] (iii) The soil temperature in a house and the field which prepared the layer (B) for each film in the atmospheric temperature sealing pipe house (frontage 5mx depth of 10m) were \*\*\*\*ed inside the house, and was spread, and the soil temperature of the daytime of summer and atmospheric temperature were measured. Soil temperature put sand into the house center section, intercepted the perimeter with the plate, set and measured the thermocouple in the location with a depth of 5cm, and showed the measured value of 14:00 at the time of fine weather with the value of external world value contrast. (It will carry out at the trial farm of Mie Prefecture in July, Heisei 8 to August) [0052] (iv) It spread inside the house by carrying out the field in which the layer (B) was prepared for each film to the cultivation nature roofing house (the frontage of 9m, the depth of 20m, 2.5m of height of ridge, 30 pitches of roof) of summer.

(a) Seeding of the spinach (form jar) was carried out to spinach each house early in July, Heisei 8, and a harvest was gathered late in August. The spinach of each house was observed from a sprout to harvest. The evaluation result was

carried out as follows.

[0053]

At 80% or more of five : germinating rates, growth is good.

60% or more of four : germinating rates -- growth -- an ordinary thing.

What has growth and \*\* poor at 40% or more of three : germinating rates.

What is poor development in 20% or more of two : germinating rates.

What has growth \*\*\*\*\* poor at 20% or less of one : germinating rates.

[0054] (b) Dendrobium (two-year stock) was carried in to Dendrobium each house early in June, Heisei 8, and it observed the growth after \*\*\*\*, and with the flower early in December. The evaluation result was carried out as follows.

What has 95 good% or more of five : survival \*\*\*\*, and growth and with a flower. [ good ]

What has 85% or more of four : survival \*\*\*\*, and good growth and good flower and \*\*.

75% or more of three : survival \*\*\*\*, and growth and with a flower -- an ordinary thing.

What has 65% or more of two : survival \*\*\*\*, and poor growth and poor flower and \*\*.

The thing of 65% or less of one : survival \*\*\*\*, and a growth and a defect with a flower.

[0055]

[Table 4]

表 - 4

No 評価結果	実施例								比較例							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
フィルム No	2	1	3	4	5	6	7	8	4	5	9	9	9	10	11	12
層(A) No	M	N	M	M	N	M	M	M	P	O	M	N	-	-	-	-
層(B) No	B	A	C	D	E	F	G	H	D	E	-	-	-	-	-	-
可視光線透過率 [%]	85.1	84.8	85.7	86.8	86.9	85.0	85.0	86.5	66.3	68.2	85.7	85.0	90.1	91.0	90.0	88.0
日射遮断率 [%]	50.0	49.0	50.4	49.3	49.1	51.1	52.0	48.0	65.0	57.1	49.1	48.5	10.2	10.7	10.5	12.0
地温 [℃]	-8.5	-7.3	-8.5	-8.3	-8.4	-8.7	-8.4	-7.9	-4.7	-4.0	-3.9	-2.3	-0.5	-0.3	-0.3	-0.5
気温 [℃]	-4.0	-3.2	-3.3	-3.8	-3.2	-3.8	-3.7	-3.9	-1.5	-2.2	2.7	3.0	13.5	13.1	13.0	12.5
夏場栽培性 のホリ草	5	5	5	5	5	5	5	5	3	3	3	3	2	2	2	2
のデント・ビュム	5	5	5	5	5	5	5	5	3	3	3	3	2	2	2	2

[Translation done.]